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The Photoconductivity of Poly(*N*-vinylcarbazole). IV.[1] The Photoconductivity of Copolymers of *N*-Vinylcarbazole with Styrene, Vinyl Acetate, and *N*-Vinylpyrrolidone[2]

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In a previous paper,[1] the present authors proposed a mechanism of carrier migration in a poly-*N*-vinylcarbazole (PVCz) film based mainly on the structure of the polymer. The carriers seem to move easily along the chain from a carbazyl group to another adjacent carbazyl group through the overlap of the π-electrons of the carbazyl rings in the same polymer chain. In this note we wish to report that this manner of carrier migration is also suggested by an examination of the photoconductivity of the copolymers of *N*-vinylcarbazole (VCz) with styrene, vinyl acetate, or *N*-vinylpyrrolidone, as well as the alternate one-to-one copolymer of VCz and fumaronitrile (FN).

Copolymers rich in VCz were prepared by radical polymerization. The polymerization was carried out in a vacuum sealed tube at 60 °C for 2.5 hr. Azobisisobutyronitrile was used as the catalyst (1 mol%), and benzene as the solvent (1 mol/l). The feed ratio of monomers (VCz/comonomer) was 9/1. The copolymers thus obtained were fractionated by benzene–xylene in order to remove the PVCz homopolymer and were then purified by repeated reprecipitations (benzene–acetone). The alternate VCz–FN copolymer was prepared as has been described elsewhere.[3] The VCz content in the copolymers was determined both by elementary analysis and by UV absorption measurements. (The following absorption coefficients were used; $\varepsilon_{345}=3500$, $\varepsilon_{331}=2950$ l/mol cm.) The preparation of a sandwich-type cell and the electrical measurements were carried out in the same manner as has been described previously.[1]

The absorption spectra (both the positions of the absorption peaks and the molar extinction coefficient per carbazole unit) of the copolymers are the same as that of PVCz in the wavelength region longer than 300 mμ, where the comonomer components have no absorption. The films used in the measurement were 15 μ thick and completely absorbed the incident light shorter than 357 mμ. The fluorescence spectra of the copolymer films were almost the same as that of a PVCz film except in the case of the alternate VCz–FN

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[1] Part III of this series; K. Okamoto, S. Kusabayashi, and H. Mikawa, This Bulletin, **46**, 2324 (1973).

[2] Presented at the 23rd Anual Meeting of the Chemical Society of Japan (April, 1970).

[3] Y. Shirota, A. Matsumoto, and H. Mikawa, *Polymer J.*, **3**, 643 (1972).

Table 1. Photocurrents of the copolymers of VCz

Polymer	Magnitude of the photocurrent, $\times 10^{-13}$A/cm^2					
	with negative electrode illumination			with positive electrode illumination		
	330mμ	360mμ	400mμ	330mμ	360mμ	400mμ
PVCz	120	900	35	300	2000	80
VCz–Vinyl acetate	24	120	7	—	—	—
(8 mol%)	(1/5)	(1/7.5)	(1/5)			
VCz–Vinyl acetate	7.7	58	3.5	—	—	—
(17 mol%)	(1/16)	(1/15)	(1/10)			
VCz–Vinylpyrrolidone	4.4	42	0.6	12	60	1.6
(20 mol%)	(1/25)	(1/22)	(1/60)	(1/25)	(1/32)	(1/50)
VCz–Styrene	17	130	2.3	23	290	8.0
(15 mol%)	(1/7)	(1/7)	(1/15)	(1/13)	(1/7)	(1/10)
PVCz doped with polystyrene	56	540	20	160	800	35
(15 mol%)	(1/2)	(1/1.6)	(1/1.7)	(1/2)	(1/2.5)	(1/2.3)
Alternate 1:1 copolymer of VCz and FN	0	0	0	0	0	0

Values in parentheses represents the factors of decrease in the photocurrent as compared with the photocurrent of PVCz.

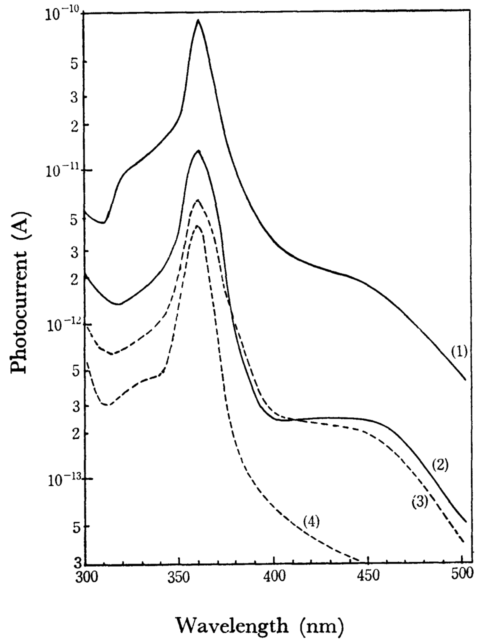

Fig. 1. Photocurrent of the copolymers of VCz with negative electrode illumination.
(1) PVCz, (2) VCz–styrene (15 mol%) copolymer, (3) VCz–vinyl acetate (17 mol%) copolymer, (4) VCz–*N*-vinylpyrrolidone (20 mol%) copolymer.

copolymer. In the film of the alternate copolymer, the excimer fluorescence was quenched almost completely and a weak emission due to the exciplex was observed.

The photocurrent was measured in a Nesa-Polymer-Gold sandwich-type cell (area of electrode: 1 cm^2) under 7000 V/cm in a high vacuum under the illumination of monochromatic light (2×10^{13} photons/cm^2 sec) at 20 °C. The copolymer films showed photoconductive properties similar to those observed in a PVCz film.1) As is shown in Fig. 1 and Table 1, however, the photocurrent of the films of the copolymers (VCz content, 92—80 mol%), was smaller in magnitude by a factor of 5—50 than the photocurrent of the PVCz film. The photocurrent decreased in all spectral regions, irrespectively of the polarity of the illuminated electrode. The reduction of the photocurrent occurred in every copolymer, independently of the kind of comonomer. The alternate VCz–FN copolymer does not show any photoconductivity, although the FN component is thought to favor the formation of the cation of carbazole chromophore. The amount of decrease in the photocurrent depends mainly on the content of the comonomer.

On the other hand, the photocurrent in the PVCz film doped with polystyrene (dope amount, 15 mol%) decreased by only a factor of 1.5—2.5 as compared with the photocurrent in an undoped PVCz film. This decrease in the photocurrent is much smaller than that of the photocurrent in the VCz–styrene copolymer with the same content of the styrene component (15 mol%).

As has been reported in the previous paper,1) the large photoconductivity of PVCz can be attributed both to the extrinsic carrier generation by the interaction of an exciton with some impurity and to the carrier migration through the overlap of π-electrons of the carbazyl groups in the same polymer chain. It has been found, from the study of the energy transfer,4) that, in the films of the VCz-rich copolymers, the number of the carbazyl groups covered by an exciton during its lifetime is limited by the excimer-forming site in the copolymer chain in the same manner as in PVCz; it is evaluated to be almost the same (700) as in a PVCz film. Assuming that the conditions of the impurity (density and distribution) are almost the same in the copolymer films and in a PVCz film, the probability of an exciton interacting with any impurity will, therefore, be almost the same in both films. Consequently, the efficiency of the extrinsic carrier generation is not expected to decrease sufficiently to explain the observed results in the films of the copolymers rich in VCz. The comonomer components such as styrene may not be anticipated to act as trap centers or recombination

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4) K. Okamoto, A. Yano, S. Kusabayashi, and H. Mikawa, Preprint of the 24th Anual Meeting of the Chemical Society of Japan, I-p. 142 (April, 1971). To be published in this *Bulletin*.

centers in view of the doping effect of some aromatic compounds on the photoconductivity of PVCz.[5] It seems, therefore, to be difficult to consider the significant decrease in the lifetime of the carrier due to trapping effect of the comonomer in the copolymer films.

Judging from the correlation between the crystallinity and the photocurrent in a PVCz film,[1] a small decrease in the crystallinity of the films does not seem to decrease the photocurrent significantly. As there was no significant difference in the crystallinity between the untreated films of the copolymers and of PVCz, the considerable decrease in the photocurrent in the films of the copolymers seems not to be due to any change in the crystallinity.

Therefore, the significant decrease in the photocurrent in the copolymers does not seem to be due to the lowering of the efficiency of the extrinsic carrier generation nor to the lowering of the crystallinity, but to the interruption effect of the comonomer components on the carrier migration. In the case of the copolymer of VCz with a comonomer such as styrene, with a small π-electron system, the sequence of the overlap of the adjacent carbazyl groups in the same polymer chain is frequently interrupted by the comonomer units introduced. As the lifetime of the carrier will be shorter than that of the exciton because of its higher energy state, it is supposed that during its lifetime a carrier covers a smaller number of the carbazyl groups than does an exciton. The excimer-forming site is hardly thought to limit the carrier migration, although it is able to act as a carrier trap. The carrier migration is, therefore, directly affected and reduced by the interruption of the overlap of the π-electrons of the carbazyl groups due to the comonomer component. This is the reason for the significant decrease in the photocurrent in the copolymers. This is also supported by the following three facts. First, as has been described previously, the decrease in the photocurrent of the copolymers does not depend on either the wavelength of the illuminated light, or the polarity of the illuminated electrode. Secondly, the decrease in the photocurrent in the PVCz film doped with polystyrene was not so large as in the film of the VCz–styrene copolymer. Thirdly, the alternate VCz–FN copolymer, where there is no sequence of carbazyl groups in the same polymer chain, has no primary photocurrent.

In conclusion, the photocurrent of the copolymers is reduced by a factor of 5—50. This might be due to the sum of the following three effects; the lowering of the efficiency of carrier generation, the reduction of the carrier life-time, and the disturbance of the carrier migration. The predominant effect seems to be the third effect, that is, the disturbance of carrier migration due to the interruption effect of the comonomer component on the overlap of the π-electrons of the carbazyl groups.

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5) Part V of this series; K. Okamoto, S. Kusabayashi, and H. Mikawa, This Bulletin, **46**, 2613 (1973).